Total Water Measurements Using In Situ UV Fragment Fluorescence Spectroscopy in Support of CRYSTAL-FACE

Summary of Research
NASA Goddard Grant NAG5-115487
Funding Period February 1, 2002–January 31, 2004

Submitted to
National Aeronautics and Space Administration from
President and Fellows of Harvard College c/o Office for Sponsored Research
Holyoke Center, Suite 727
1350 Massachusetts Avenue
Cambridge, Massachusetts 02138

James G. Anderson, Principal Investigator
Division of Engineering and Applied Sciences and
Department of Chemistry and Chemical Biology
Harvard University
12 Oxford Street
Cambridge, MA 02138

Total Water Measurements using In Situ UV Fragment Fluorescence Spectroscopy in Support of CRYSTAL-FACE. NASA Goddard Grant NAG5-11547

Summary of Research. Funding period February 1, 2002-January 31, 2004

Given both the powerful diagnostic importance of the condensed phases of water for dynamics and the impact of phase changes in water on the radiation field, the accurate, in situ observation of total water is of central importance to CRYSTAL-FACE. This is clear both from the defined scientific objectives of the NRA and from developments in the coupled fields of stratosphere/troposphere exchange, cirrus cloud formation/removal and mechanisms for the distribution of water vapor in the middle/upper troposphere. Accordingly, we were funded under NASA Grant NAG5-115487 to perform the following tasks for the CRYSTAL-FACE mission that took place in Key West, Florida, during July 2001:

- 1. Prepare the Total Water instrument for integration into the WB57F and test flights scheduled for Spring 2002.
- 2. Calibrate and prepare the Total Water instrument for the Summer 2002 CRYSTAL-FACE science flights based in Jacksonville, Florida.
- 3. Provide both science and engineering support for the above-mentioned efforts.
- 4. Analyze and interpret the CRYSTAL-FACE data in collaboration with the other mission scientists.
- 5. Attend the proposed science workshop in Spring 2003.
- 6. Publish the data and analysis in peer-reviewed journals.

Field Performance

The total water instrument performed successfully on the NASA WB-57F research aircraft during the three test flights in May 2002 from Ellington Air Force Base, Houston, Texas, part of the ferry flight from Houston to Key West, Florida, and the 12 science flights in July 2002 from Key West Naval Air Station in Key West. Instrument performance and accuracy is critical for this instrument because the goal of virtually every science flight was to make quantitative measurements of the microphysical properties of the ice particles in cirrus clouds that have evolved from local convective storms. Accordingly, in addition to the preflight laboratory calibrations performed at Harvard, laboratory calibrations were carried out in both the Ellington Field and Key West Naval Station hangars. All the total water mixing ratios, along with ice water content were archived using preliminary calibration data for use by other experimenters on the CRYSTAL FACE mission. Final laboratory post-flight calibrations are currently taking place and final data will be archived shortly.

Additionally, measurements in clouds, during which the measured water vapor signal increases significantly for a short period of time, offers a unique opportunity to compared water vapor measured by absorption in flight with water vapor measured by photofragment fluorescence using laboratory calibration data. We show an example of this in figure 1 below. Taken during the flight of 20020709, agreement between water vapor measured by absorption is better than 5%. This plot is a typical example of more than 25 opportunities to make this comparison during the CRYSTAL FACE campaign.

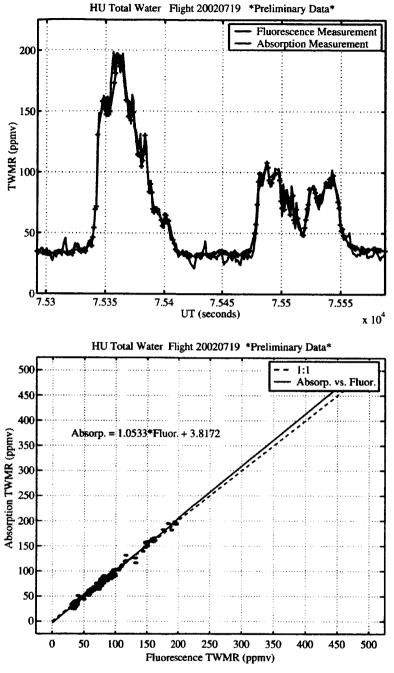


Figure 1. Comparison of water vapor measured by photofragment fluorescence and by in-flight absorption during the 20020709 flight. The top panel plots the water vapor measured as measured by the two techniques while the bottom panel illustrates the quantitative agreement for the two independent determinations of water vapor mixing ratio for the part of the flight shown in the top panel.

As an example of the data quality provided, we show a plot of water vapor, total water, and the derived cloud ice content for the flight of 20020709. In the top left quadrant, a plot of the full flight is shown. In the top right quadrant, we focus in on the initial descent portion of the flight. This is instructive because within a matter of minutes we are measuring water vapor mixing ratios in the upper troposphere three orders of magnitude smaller than the initial

measurements in the lower to mid-troposphere. Consequently, hysteresis effects from instrument walls are always a concern in this region. Because the mass flow through the total water inlet is about an order of magnitude lower than through the water vapor instrument, comparing the two instruments at the beginning of the flight provides a very sensitive look at hysteresis. Using this section of the flight, we illustrate that quantitative detection of small amounts of ice is viable even on ascent. In the bottom left quadrant we focus in on a large cloud event. This plot also shows that there is no detectable hysteresis in the total water instrument after the aircraft passed through the cloud. In the bottom right quadrant we illustrate four brief cloud incursions with the two instruments tracking perfectly in clear air outside the cloudy regions. More thorough discussion and examples of data quality are illustrated in the preprint included in the appendix of this report.

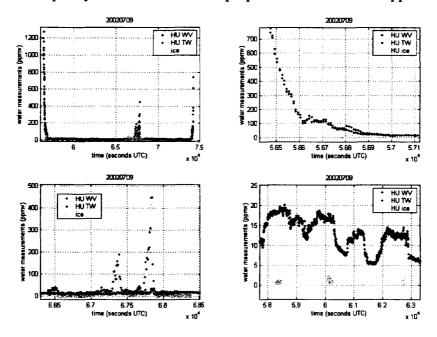


Figure 2. Measurements of water vapor, total water and cloud water content on the 20020709 flight of the WB-57F during CRYSTAL FACE. The top left quadrant shows the full flight, while the other three focus on different segments of the mission as described in the text.

Data Analysis and Interpretation

During year two of the funding period, we participated in the CRYSTAL-FACE science meeting in Salt Lake City, UT, as well as American Geophysical Society meetings in Nice, France, in April 1993 and in San Francisco, CA, in December 2003. These presentations focused on validation of the total water instrument and on the intercomparison of cirrus cloud ice water content measured *in situ* with the Harvard water vapor and total water instruments on the WB-57 with that measured remotely from the ER-2 aircraft using 94 GHz radar reflectivity. We include as appendices preprints of papers covering these two issues. A summary of the major conclusions from these two papers follows.

Controversy that has surrounded the accuracy of *in situ* water vapor measurements in the stratosphere and upper troposphere was summarized in the December 2000 "SPARC Assessment of Upper Tropospheric and Stratospheric Water Vapour." That prompted attempts at further water intercomparisons. In our view, water vapor measurement accuracies required to resolve the scientific questions in the UT/LS in the context of global climate change leave little doubt that a

"benchmark" water vapor instrument is needed. Multiple *in situ* intercomparisons of water measured by absorption and fluorescence by the total water instrument, facilitated by total water variability in cloud regions, move us a step closer to achieving benchmark requirements when both instruments are making simultaneous measurements.

Accurate in situ water measurements require (1) a carefully calibrated detection method, and (2) proof that the water vapor mixing ratio in the detection region is the same as in ambient air. Simultaneous measurements of water vapor in clear using both the total water and water vapor instruments provide additional evidence for both of these. Regarding the first issue, while the two instruments are identically calibrated, uncertainties in the calibration arise mostly from optical deterioration during field missions, not in the uncertainty of the calibrations themselves. Accordingly, agreement in the two measurements limits that uncertainty. Regarding the second, because the two instruments utilize very different ducting and flow velocities to carry the air from their respective inlets to their detection axes, agreement between the two measurements validates this aspect of instrument design, an especially critical issue for total water using an isokinetic inlet.

One of the critical goals of the CRYSTAL FACE (CF) mission was to perform intercomparisons of *in situ* cirrus ice water content (IWC) measurements taken on the WB-57 with remote measurements from the ER-2 using the Goddard remote Cloud Radar System (CRS). In support of this goal, ER-2 and WB-57 flight tracks were synchronized to maximize measurements of the same cirrus clouds by both instruments. However, initial studies have shown that in order to ensure sufficient overlap of the two measurements the instruments must sample air within a few kilometers of each other. This was rarely accomplished during CF. While instruments on the two aircraft were able to sample the same space, differences in sampling times meant that they were not actually sampling the same air parcel. The exact spatial and temporal requirements depend upon the level of inhomogeneity within the cloud. Therefore, it is necessary to investigate, based on cloud inhomogeneities, the statistics necessary to perform a valid intercomparison within a cloud system that is not sampled simultaneously by the remote and *in situ* instruments. We have initiated a program to use cloud microphysical models to investigate this problem.

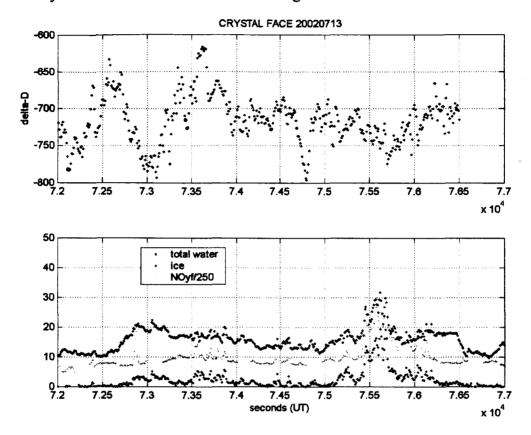
Cloud ice water content measurements are needed for understanding various aspects of cloud microphysics and the radiative properties of these clouds. The two papers referenced below, published using CRYSTAL FACE data, require ice water content measurements to relate cloud extinction to ice water content (Garrett et al.) and to investigate the effective density of ice particles as a function of particle size distribution (Heymsfeld et al.).

Garrett, T. J., H. Gerber, D. G. Baumgardner, C. H. Twohy, and E. M. Weinstock, "Small, highly reflective ice crystals in low-latitude cirrus," *Geophys. Res. Lett.* 30, doi:10.1029/2003GL018153, 2003.

Heymsfield, A. J., C. G. Schmitt, A. Bansemer, D. Baumgardner, E. M. Weinstock, J. T. Smith, and D. Sayres, "Effective ice particle densities for cold anvil cirrus," *Geophys. Res. Lett.* 31, doi:10.1029/2003GL018311, 2004.

While the total water measurements are typically utilized along with water vapor to determine ice water content, the total water measurement itself is a valuable tracer. This is especially true when trying to identify the origin of thin cirrus in the tropopause region. Total water measurements can distinguish between cirrus from anvil blowoff and cirrus formed in situ, because total water should be conserved when a cloud is formed in situ. For example, during the

flight of July 13, 2002, Webster and Heymsfeld (*Science* 302, 1742-5, 2003) use the invariance of total water isotopic water measurements to identify a cirrus cloud as one formed *in situ*. We show the utility of total water measurements in the figure below.



In this plot we show delta-D in the top panel, representing the total water isotope ratio, with the fairly narrow range of values indicating stratospheric air. The authors suggested that the invariance of delta-D through the cloud identifies the cloud as formed *in situ*. While there are a number of cloud features in the figure, the most significant is just past 75000 seconds, and it illustrates that neither total water nor total NOy, (NOyf), is conserved. This is inconsistent with a cloud formed *in situ*.

Analysis of CRYSTAL FACE data water and total water data is continuing, and both the accuracy issues and intercomparisons with remote ice water measurements are an important part of our participation in the April/May 2004 MidCiX mission.

Appendices:

Weinstock, E. M., J. B. Smith, D. Sayres, J. V. Pittman, N. Allen, J. Demusz, M. Greenberg, M. Rivero, J. G. Anderson "Measurements of the Ice Water Content of Cirrus in the Tropics and Subtropics I: Instrument Details and Validation," J. Geophys. Res., in preparation, 2004
Sayres, D. S., J. V. Pittman, J. B. Smith, E. M. Weinstock, J. G. Anderson, G. Heymsfield, L. Li, A. Fridlind, and A. S. Ackerman, "Methods for Validation and Intercomparison of Remote Sensing and In situ Ice Water Measurements: Case Studies from CRYSTAL-FACE and Model Results," Geophys. Res. Lett., in preparation, 2004.